The first metal complexes of 3,3'-bi-1,2,4-oxadiazole: a curiously ignored ligand.

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Abstract

The crystal structure of 3,3'-bi-1,2,4-oxadiazole (**1**) reveals a planar centrosymmetric structure for this molecule in the solid state. It forms a mononuclear complex (**3**) with palladium(II) chloride, which is shown by X-ray crystallography to contain the ligand chelated through the two N4 nitrogens. The X-ray structure of the complex (**5**) with silver(I) nitrate shows a one-dimensional coordination polymer in which the ligand acts in a bridging mode, again with coordination through the N4 nitrogen atoms.

Keywords: 1,2,4-Oxadiazole; Palladium; Silver; N Ligands

We have long been involved in the synthesis and study of metal complexes of heterocyclic ligands [1]. In particular, we have focused on the design of ligands incorporating less commonly studied heterocyclic ring systems, such as tetrazoles [2],1,2-benzisoxazoles [3], furoxans [4], benzotriazoles [5,6], 1,4,2,5-dioxadiazines [7], thiazolo[5,4-d]thiazoles [8], 1,2,3-thia(and selena)diazoles [9], pyridazines [10], 1,2,5-oxadiazoles and 1,2,5-thiadiazoles [11,12]. Within this context, we noted that 1,2,4-oxadiazoles have been curiously ignored as subcomponents within ligands, be they monodentate, chelating or bridging. Indeed, a search of the Cambridge Crystallographic Database revealed that only three papers reported metal complexes of ligands containing a 1,2,4-oxadiazole subunit [13-15].

In continuation of our interest in the chemistry of biheterocycles [16], we realised that of the three isomeric bi-1,2,4-oxadiazoles, the 3,3'-isomer (**1**) represents a particularly interesting potential ligand. This compound has been known for over forty years [17] and could potentially chelate to a single metal in any of three modes (Fig. 1, (a)-(c)) and, furthermore, offers the possibility of bridging two metals in either of two ways (Fig.1, (d)-(e)). Curiously however, it has never been used as a ligand in coordination or metallosupramolecular chemistry. We therefore set out to explore the use of this compound as a ligand and herein describe the synthesis and X-ray crystal structures of the free ligand, a mononuclear palladium(II) complex and a one-dimensional silver(I) coordination polymer.

[Fig. 1 here]

3,3'-Bi-1,2,4-oxadiazole (**1**) was prepared in 76% yield by a double cyclisation of oxamidoxime (Scheme 1), based on a literature procedure [18]. In order to confirm unambiguously its structure and to examine the conformation of the ligand in the solid state we determined the X-ray crystal structure of **1** [19]. It crystallises in the orthorhombic space group Cmca with a mere quarter of the molecule in the asymmetric unit; the whole molecule lies on a crystallographic mirror plane and also resides upon a crystallographic centre of inversion (Fig. 2). As such the molecule is perfectly planar and centrosymmetric, a situation that we have previously proposed to be favoured for symmetrical biheterocycles for the

reason that this eliminates any dipole moment and facilitates maximal π-π stacking of the molecules in the solid state [20].

[Scheme 1 and Fig. 2 here]

We next proceeded to explore the coordination chemistry of **1** by preparing a mononuclear complex. We chose palladium(II) as the metal, based on a long standing affection for this well-behaved, square-planar metal synthon [21]. Our first attempt to prepare a palladium complex of **1** involved reaction with $PdCl_2$ in 2M HCl solution. This reaction furnished crystals of a product that we were able to identify as the ring-opened hydrolysis derivative **2** (Scheme 1), on the basis of a preliminary X-ray crystal structure determination of a highly twinned crystal. This result is in keeping with an early report that 1,2,4-oxadiazoles are prone to acid-catalysed ring-opening reactions [17]. Thus, we next reacted **1** with Li_2PdCl_4 under neutral conditions and, pleasingly, this produced a complex (**3**) with an intact ligand in good yield (Scheme 1) [22].

This complex crystallises in the orthorhombic space group Pbca, with a full molecule in the asymmetric unit (Fig. 3) [23]. It consists of a $PdCl_2$ unit bound to the two N4 nitrogens of the ligand (i.e. mode (b) in Fig. 1). The values for the bond lengths and angles within the 1,2,4-oxadiazole rings in this complex are similar to those reported in the other coordination complexes of ligands containing a 1,2,4-oxadiazole rings [13-15] and to those of the free ligand **1**. As expected the palladium atom has square planar geometry, the largest deviation from idealized geometry being due to the presence of the five-membered chelate ring. The two rings of the chelating ligand are almost coplanar (angle between meanplanes = 1.5 ^{o}).

[Fig. 3 here]

Given that this complex might be further induced to coordinate to another metal, attempts were made to prepare a binuclear complex (such as **4**, Scheme 1) by reaction of **1** with excess Li_2PdCl_4. All such reactions produced only the mononuclear complex **3**.

Having demonstrated that 3,3'-bi-1,2,4-oxadiazole (**1**) can form discrete mononuclear complexes, we next investigated the use of this ligand for the preparation of metallosupramolecular assemblies. On the basis of the potential of this molecule to act as a

bridging ligand and given the current interest in the employment of silver(I) synthons for the preparation of coordination polymers [24-31], we reacted **1** with silver nitrate. This furnished a crystalline product (**5**) in 69% yield [32]. It crystallises in the orthorhombic space group Pnma [33] with half a molecule of **1** and half a silver nitrate moiety in the asymmetric unit (Fig. 4).

[Fig. 4 here]

The silver nitrate unit lies on a crystallographic mirror plane, while the bioxadiazole lies on a crystallographic centre of inversion. The silver atom has a distorted trigonal geometry and is coordinated to a monodentate nitrate and the N4 nitrogen of two different molecules of **1**. Thus the ligand now acts in a bridging (divergent) mode, rather than the chelating (convergent) mode of complex **3**. This, therefore, leads to a one-dimensional coordination polymer, a section of which is shown in Fig. 5. Due to the presence of the centre of inversion, the rings of the ligand are strictly coplanar and *transoid*. The two symmetry elements provide this one-dimensional metallopolymer with a central axis, about which the nitrate anions oscillate with the polymer itself weaving about in a wave-like fashion.

[Fig. 5 here]

On the basis of the preliminary results described above, it appears that ligand **1** prefers to coordinate through the N4 nitrogens of the 1,2,4-oxadiazole rings. The reasons for this are uncertain, but are probably associated with the greater basicity of the N4 nitrogen donors compared to the N2 atoms. Support for this comes from the fact that, in all eight previously reported X-ray crystal structures of metal complexes of ligands containing a 1,2,4-oxadiazole ring, coordination occurs preferentially through the N4 nitrogen [13-15]. This aspect will be the subject of future studies.

Acknowledgements

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Supplementary material

Crystallographic data for **1, 3** and **5** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 642333 - 642335). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at:doi:10.1016/j.inoche.xxxx.

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[19] Crystallographic data for **1**: $C_4H_2N_4O_2$, Fw 1138.10, orthorhombic, Cmca, a = 6.187(6), b = 7.693(7), c = 11.535(11) Å, V = 549.0(9) $Å^3$, Z = 4, F(000) = 280, Bruker CCD area detector, T = 168(2) K, colourless block, 0.74 x 0.33 x 0.23 mm, μ = 0.139 mm^{-1},

D_x = 1.671 g cm^{-3}, 2θ-range 3-50 °, 265 unique reflections, 247 with I > 2σ(I), 32 parameters, wR (all data) 0.082, R_1 [I > 2σ(I)] 0.031.

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[22] Preparation of **3**: 3,3'-bi-1,2,4-oxadiazole (66 mg, 0.48 mmol) dissolved in MeOH (2.5 mL) was added to a methanolic solution of 0.0942 M Li_2PdCl_4 (5.2 mL, 0.49 mmol). After evaporation of *ca*. half the solution, orange plates formed and these were collected by filtration (35 mg). Further solid was obtained after more evaporation of the filtrate and this too was collected by filtration (60 mg). Yield 95 mg (63%), m.p. >300°C (Found: C, 15.15; H, 0.46; N, 17.96; Cl, 23.06. $C_4H_2N_4Cl_2O_2Pd$ requires: C, 15.23; H, 0.62; N, 17.76; Cl, 22.48).

[23] Crystallographic data for **3**: $C_4H_2Cl_2N_4O_2Pd$, Fw 315.40, orthorhombic, Pbca, a = 7.7176(4), b = 13.1725(6), c = 16.5280(8) Å, V = 1680.2(1) $Å^3$, Z = 8, F(000) = 1200, Bruker CCD area detector, T = 153(2) K, orange plate, 0.40 x 0.31 x 0.04 mm, μ = 2.812 mm^{-1}, D_x = 2.494 g cm^{-3}, 2θ-range 5-47 °, 1212 unique reflections, 1048 with I > 2σ(I), 120 parameters, wR (all data) 0.049, R_1 [I > 2σ(I)] 0.025.

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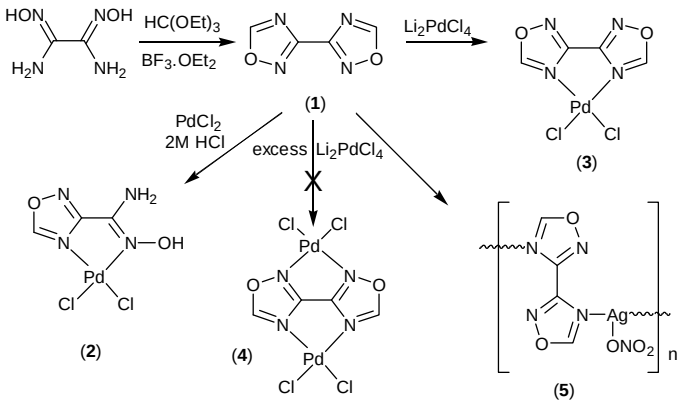
[32] Preparation of **5**: 3,3'-bi-1,2,4-oxadiazole (20 mg, 0.15 mmol) dissolved in MeOH (1 mL) was added to $AgNO_3$ (31 mg, 0.15 mmol) dissolved in MeOH (1 mL) and H_2O (3–

4 drops). A white solid formed immediately and was collected by filtration. Recrystallisation from acetonitrile produced crystals suitable for X-ray diffraction. Yield 35 mg (69%), m.p. 141–145°C (Found: C, 15.70; H, 0.39; N, 22.69. $C_4H_2N_5O_5Ag$ requires: C, 15.60; H, 0.65; N, 22.74).

[33] Crystallographic data for **5**: $C_4H_2AgN_5O_5$, Fw 307.98, orthorhombic, Pnma, a = 10.0248(10), b = 14.7795(11), c = 5.3288(5) Å, V = 789.52(12) $Å^3$, Z = 4, F(000) = 592, Nicolet P4s diffractometer, T = 153(2) K, colourless prism, 0.78 x 0.42 x 0.21 mm, μ = 2.567 mm^{-1}, D_x = 2.591 g cm^{-3}, 2θ-range 3-54 °, 895 unique reflections, 854 with I > 2σ(I), 77 parameters, wR (all data) 0.069, R_1 [I > 2σ(I)] 0.026.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NOH
H2N
NH2
HC(OEt)3
BF3.OEt2
(1)
Li2PdCl4
(3)
PdCl2
2M HCl
excess Li2PdCl4
(2)
(4)
(5)
Pd
Cl
N
O
Ag
ONO2
n

Scheme 1.

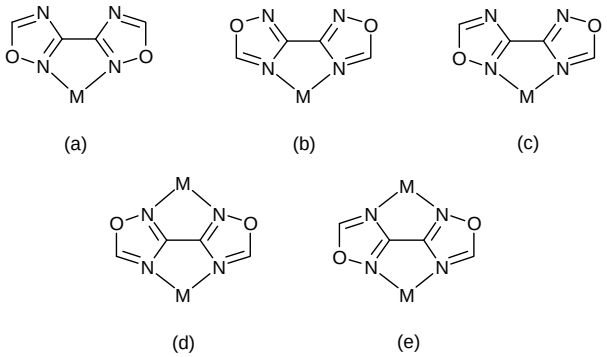

Fig. 1. The five potential coordination modes of 3,3'-bi-1,2,4-oxadiazole (**1**): (a) and (b) symmetrical mononuclear, (c) unsymmetrical mononuclear, (d) unsymmetrical binuclear and (e) symmetrical binuclear.

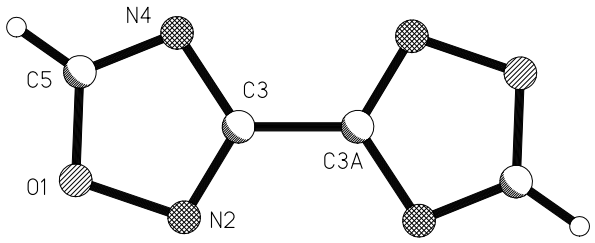

Fig. 2. Perspective view, with atom labelling of the contents of the asymmetric unit, of **1**. Selected bond lengths (Å) and angles (°): O1-C5 1.327(2), O1-N2 1.403(2), N2-C3 1.292(2), C3-N4 1.373(2), N4-C5 1.282(2), C3-C3A 1.457(3), C5-O1-N2 106.6(1), C3-N2-O1 102.2(1), N2-C3-N4 115.7(1), C3-N4-C5 101.4(1), N4-C5-O1 114.1(2).

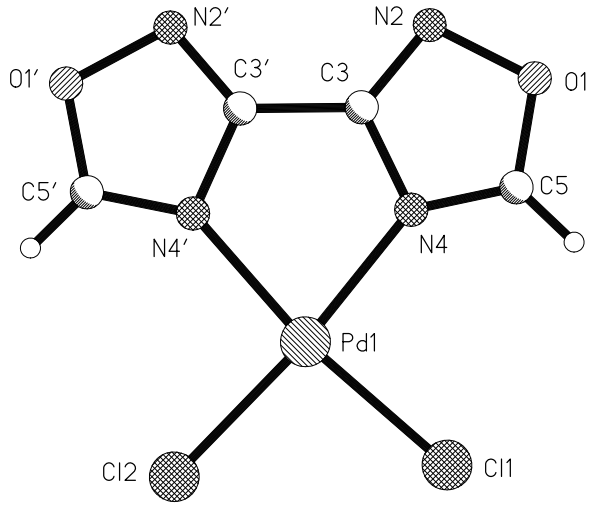

Fig. 3. Perspective view, with atom labelling of the contents of the asymmetric unit, of **3**. Selected bond lengths (Å) and angles (°): Pd1-N4 2.031(3), Pd1-N4' 2.046(3), Pd1-Cl1 2.270(1), Pd1-Cl2 2.277(1), N4-Pd1-N4' 79.8(1), Cl1-Pd1-Cl2 92.82(3), O1-C5 1.335(4), O1'-C5' 1.335(4), O1-N2 1.417(4), O1'-N2' 1.423(4), N2-C3 1.295(4), N2'-C3' 1.290(5), C3-N4 1.372(5), C3'-N4' 1.386(4), N4-C5 1.289(4), N4'-C5' 1.298(5), C3-C3’ 1.461(5), C5-O1-N2 107.6(3), C5'-O1'-N2' 107.4(3), C3-N2-O1 102.0(3), C3'-N2'-O1' 102.3(3), N2-C3-N4 115.0(3), N2'-C3'-N4' 115.3(3), C3-N4-C5 103.5(3), C3'-N4'-C5' 102.6(3), N4-C5-O1 111.9(3), N4'-C5'-O1' 112.5(3).

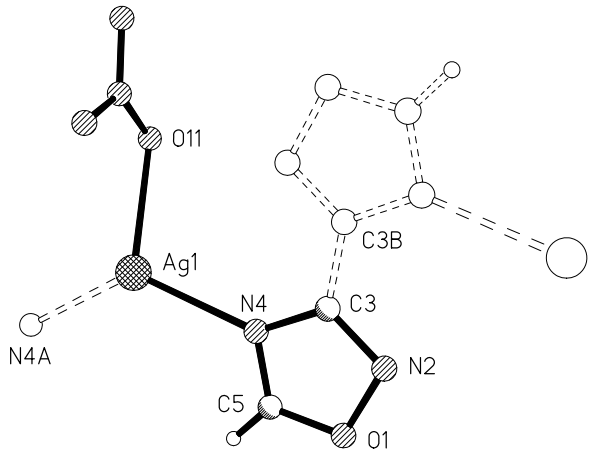

Fig. 4. Perspective view, with atom labelling of the contents of the asymmetric unit, of **5**. Selected distances (Å) and angles (°): Ag1-N4 2.384(2), Ag1-O11 2.369(3), O1-N2 1.417(3), N2-C3 1.309(3), C3-N4 1.384(3), N4-C5 1.301(3), C3-C3B 1.478(5), O11-Ag1-N4 111.33(5), N4-Ag1-N4A 131.82(9), C5-O1-N2 106.6(2), C3-N2-O1 102.6(2), N2-C3-N4 115.2(2), C3-N4-C5 102.0(2), N4-C5-O1 113.6(2).

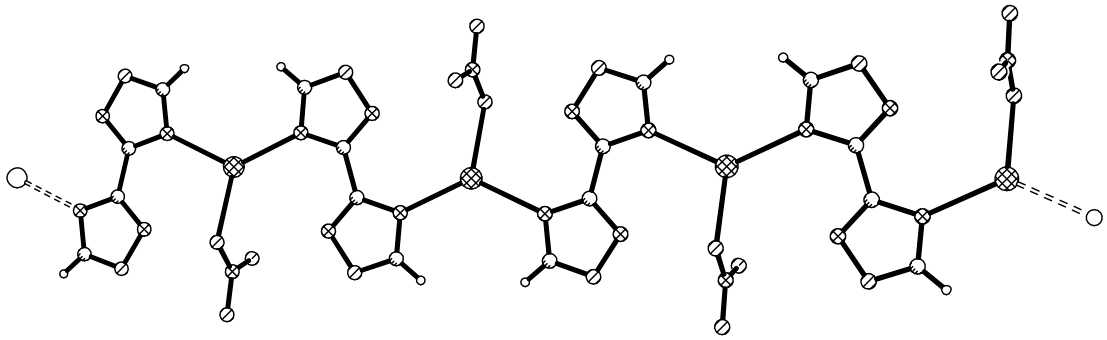

Fig. 5. View of the extended 1D polymeric structure of **5**.